

# PATENT SPECIFICATION

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## (54) TREATMENT OF ACID WASTE WATER CONTAINING CYANURIC ACID AND/OR AMINOTRIAZINES BY HYDROLYSIS

(71) We, FMC CORPORATION incorporated and existing in the State of Delaware, United States of America, of 2000 Market Street, Philadelphia, State of Pennsylvania 19103, United States of America, (assignee of SIDNEY BERKOWITZ and CHARLES VINCENT JUELKE), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to a high pressure thermal hydrolysis process which effects fast and efficient decomposition of cyanuric acid and amino-substituted triazines contained in acid waste water streams from the production of cyanuric acid and chlorinated derivatives of cyanuric acid.

Cyanuric acid and chlorinated derivatives of cyanuric acid are commercially produced in multi-million pound quantities. Dichloroisocyanuric acid and trichloroisocyanuric acid and alkali metal salts of dichloroisocyanuric acid are well known as a source of active chlorine. They are widely used to treat water supplies to prevent the growth of pathogenic bacteria and are used in detergent, bleaching, and sanitizing compositions. Acid waste water streams from plants producing these materials contain cyanuric acid and on occasion, dissolved amino-substituted triazines, namely, ammeline, ammelide and melamine. During upset conditions, undissolved cyanuric acid may be present in the waste water streams.

The acid digester waste water stream is the largest source of carbonaceous and nitrogenous pollutants. This stream results from the purification of crude cyanuric acid by hydrolysis with an acid, as for example, sulfuric acid. Crude cyanuric acid contains approximately 80% cyanuric acid and approximately 20% amino-substituted triazines. Amino-substituted triazines are hydrolyzed to cyanuric acid, most of which is recovered by filtration. The waste filtrate has a pH of from 0 to 3 and contains

from 0.2% to 2% by weight cyanuric acid as well as up to 2.5% by weight unhydrolyzed amino-substituted triazines.

Hydrogen peroxide treated waste water streams result when hydrogen peroxide is employed to treat waste chlorination liquors resulting from the production of dichloroisocyanuric acid, trichloroisocyanuric acid, and alkali metal salts of dichloroisocyanuric acid. (U.S. Patent No. 3,878,208 granted April 15, 1975). Upon treatment with hydrogen peroxide, dechlorination results and most of the cyanuric acid is recovered by filtration. The remaining waste filtrate has a pH of from 0.5 to 3, when cyanuric acid is to be recovered, or from 6 to 10, when alkali metal salts of cyanuric acid are to be recovered. In most instances, the acid range is selected and the waste filtrate contains from 0.03% by weight to 0.05% by weight of dissolved cyanuric acid.

The various waste water streams containing cyanuric acid and amino-substituted triazines may be combined for disposal, and in view of the relatively large amount of acid digester waste water stream any combined stream requiring disposal will be an acid stream having a pH of from 0 to 6. In addition, during upset conditions, the combined waste water stream may be a slurry containing up to 25% by weight of cyanuric acid. Such slurries result from spills of cyanuric acid occurring outside the line during the manufacture of cyanuric acid, which spills are flushed into the waste effluent.

Various methods are known in the art for decomposing cyanuric acid and amino-substituted triazines. It is known, for example, that nitrification of the ring nitrogen in cyanuric acid and in the amino-substituted triazines is effected by the action of certain bacteria. Biological degradation of cyanuric acid, while complete, requires a minimum of 6 to 9 weeks. The amino-substituted triazines are not completely degraded even after 15 weeks. (Nitrification Characteristics of Urea Pyrolyzates, Cyanurates, Melamine, and

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Related Compounds. K. G. Clark, J. Y. Yee, and T. G. Lamont, Fertilizer and Agricultural Lime Section, Soil and Water Conservation Research Division, Agricultural Research Service, U.S. Department of Agriculture, Beltsville, Maryland).

It is also known that cyanuric acid and amino-substituted triazines present in aqueous waste water streams from melamine production plants can be hydrolyzed to ammonia and carbon dioxide in alkaline solution at temperatures up to 200°C. (V. M. Karlike et al, Kinetics of Melamine Hydrolysis, Khim Prom (Moscow) 1971, 47 (10) 784-5; USSR Patent 345,103, publication date July 14, 1972). According to the process described in this patent, waste water streams containing 1 to 2 grams per liter of cyanuric acid and amino-substituted triazines may be treated with alkali at a temperature of from 120°C to 200°C, under autogenous pressure, to effect almost complete hydrolysis of the cyanuric acid and amino-substituted triazines to form ammonia and carbon dioxide.

It is further known that amino-substituted triazines will undergo hydrolysis in acid media to produce cyanuric acid. (U.S. Patent 2,768,167). This patent describes a high pressure thermal hydrolysis process for making cyanuric acid from the amino-substituted triazines, ammeline, ammelide and melamine. The process involves heating amino-substituted triazines in sulfuric acid to temperatures of at least 175°C to 200°C. The patent further states that higher temperatures may be used but the additional advantages thereby gained are usually offset by the increased expense.

Environmental considerations make it imperative that plant effluents are produced which are substantially reduced in nitrogenous and carbonaceous pollutants. A process is, therefore, needed which will effectively and efficiently remove cyanuric acid and amino-substituted triazines from such acid waste streams.

The present invention provides a process that results in effective high pressure thermal hydrolysis of acid waste water streams containing a compound selected from cyanuric acid, melamine, ammeline and ammelide, said waste streams having a pH of from 0 to 6, which process comprises:

(a) heating said waste water streams in a pressure vessel at a temperature of from 225°C to 275°C under the autogenously developed pressure; and

(b) continuing said heating for from one minute to 15 minutes, until said compound has been hydrolyzed into ammonia and carbon dioxide.

It is most unexpected that at temperatures above about 225°C complete hydrolysis of cyanuric acid and amino-substituted triazines present in acid waste water streams, can be

effected in a matter of minutes. This effect is especially surprising in view of the large amounts of cyanuric acid, that is, up to about 25% by weight of cyanuric acid in said acid waste water streams, which can be hydrolyzed by the inventive process in such a short time.

The present invention can be carried out on aqueous waste streams having a pH from 0 to 6.

The waste stream to be treated is passed into a pressure vessel, capable of handling 1 to 30 atmospheres of pressure. The pressure used is the autogenous pressure resulting from the operating temperature selected and the amount of the materials to be hydrolyzed.

The temperature employed can range from 225°C to 275°C. The preferred range is from 245°C to 275°C. At these temperatures, complete hydrolysis can be effected in from 1 to 15 minutes, and in most instances is effected in from 1 to 5 minutes. The time required for complete hydrolysis depends more on the selected temperature than the concentration of cyanuric acid in the waste stream to be hydrolyzed. Where a higher concentration of substituted triazines, as melamine, ammeline, and ammelide is present, a higher temperature may be desired as compared to that selected for hydrolysis of waste water streams not containing these materials.

This process can effect complete hydrolysis of cyanuric acid and slurries containing up to 25% by weight of cyanuric acid to produce ammonia and carbon dioxide. In acid media, the ammonia produces ammonium salts with the acid present, as for example, ammonium bisulfate and ammonium sulfate. These salts may be recovered by conventional crystallization methods. The carbon dioxide produced is evolved as a gas.

If desired, the hydrolyzed effluent may be treated with caustic alkali, such as sodium hydroxide, to produce ammonia and sodium carbonate. The ammonia may be purged from the effluent with, for example, a stream of an inert gas or steam. The sodium carbonate may be recovered by conventional crystallization methods.

The following examples further illustrate the invention.

#### EXAMPLE I

A sample of acid digester aqueous waste stream was obtained from a commercial installation for the manufacture of cyanuric acid. Analysis of this waste stream showed that it contained 20.1% by weight sulfuric acid, 0.27% by weight cyanuric acid, 0.49% by weight ammelide, 0.13% by weight ammeline, and 4.1% by weight ammonium bisulfate. The pH of this stream was 0.5.

A 300 ml Hastelloy B autoclave was

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charged with 150 ml of this waste stream. ("Hastelloy" is a Trade Mark). The autoclave was sealed and heated with shaking to 250°C. The reaction mass was maintained at this temperature for 1 minute and then allowed to cool slowly to room temperature. The pressure employed was the autogenous pressure (pressure developed due to heating), and was recorded at 620 pounds per square inch gauge (psig) (43.59 kilograms per square centimeter gauge (kg/cm<sup>2</sup>g)).

The hydrolyzed stream was analyzed to determine the presence of cyanuric acid and amino-substituted triazines.

The melamine precipitation method used to analyze for cyanuric acid, showed a complete absence of cyanuric acid. This method involves the addition of a dilute solution of melamine to form an insoluble cyanuric acid-melamine complex, from which the amount of cyanuric acid present is gravimetrically determined. The hydrolyzed stream was further analyzed by means of ultraviolet spectroscopy to determine the presence of amino-substituted triazines. Lack of absorption in the region 200 to 250 nanometers indicated that no triazine ring structure remained.

#### EXAMPLE II

Four separate 20% slurries of cyanuric acid in distilled water (that is, 1 gram of cyanuric acid per four grams of water) were prepared, which slurries had a pH of 4.3.

A 300 ml Hastelloy B autoclave was individually charged in four runs with 150 ml of each of the above described slurries. The autoclave was sealed and heated with shaking to one of four selected temperatures, namely, 190°C, 200°C, 225°C and 250°C. Each reaction mass was maintained at the selected temperature for one minute and then allowed to cool slowly to room temperature. The pressures employed were the autogenous pressures and were recorded at 150 (10.5465), 200 (14.062), 415 (29.17865) and 900 psig (63.279 kg/cm<sup>2</sup>g), respectively.

The amounts of cyanuric acid remaining in the hydrolyzed streams were determined by the melamine precipitation method. Results set forth in Table 1, show that at a temperature of 250°C, no cyanuric acid remained in the hydrolyzed stream.

#### EXAMPLE III

Four separate 20% slurries of cyanuric acid in 20% phosphoric acid, (that is, one gram of cyanuric acid per four grams of 20% phosphoric acid), were prepared, which slurries had a pH of 0.7.

The hydrolysis procedure followed was identical to that described for Example II. The autogenous pressures corresponding to the temperatures 190°C, 200°C, 225°C, and 250°C, were recorded as 150 (10.5465), 200 (14.062), 415 (29.17865), and 900 psig (63.279 kg/cm<sup>2</sup>g), respectively.

The amounts of cyanuric acid remaining in the hydrolyzed stream were determined by the melamine precipitation method. The results set forth in Table II show that at a temperature of 250°C no cyanuric acid remained in the hydrolyzed stream.

#### EXAMPLE IV

A 20% slurry of crude cyanuric acid, (assay 80% cyanuric acid, 18% ammelide, 2% ammeline), in 20% phosphoric acid (one gram of crude cyanuric acid per four grams of 20% phosphoric acid), was prepared, which slurry had a pH of 0.5.

Hydrolysis was carried out at 250°C, following the procedure described above for Example II. The autogenous pressure was recorded at 900 psig.

Analysis of the hydrolyzed stream for cyanuric acid by the melamine precipitation method, and for triazine ring structure by ultraviolet spectroscopy, indicated the complete absence of cyanuric acid and amino-substituted triazines.

#### EXAMPLE V

A simulated hydrogen peroxide treated waste stream was prepared by dissolving 320 grams of sodium chloride and 4.5 grams of sodium sulfate in 3,416.9 grams of distilled water. 22.9 grams of cyanuric acid were added to the solution and the mixture was stirred for one hour. 7.1 grams of sodium hydroxide and 150 grams of distilled water were then added to the mixture. The resulting slurry was stirred for 6 hours, allowed to stand overnight, and the solids were removed by filtration. Analysis of the filtrate by the melamine precipitation method showed that it contained 0.05% by weight cyanuric acid. The initial pH of this solution, 7.3, was adjusted to 4.2 by the addition of hydrochloric acid.

A 300 ml Hastelloy B autoclave was charged with 150 ml of this simulated waste stream. The autoclave was sealed and heated with shaking to 275°C. The reaction mass was maintained at this temperature for one minute and then allowed to cool slowly to room temperature. The autogenous pressure was recorded at 750 psig (52.7325 kg/cm<sup>2</sup>g).

The melamine precipitation method showed a complete absence of cyanuric acid in the hydrolyzed stream.

TABLE I  
Decomposition of 20% Slurries of  
Cyanuric Acid in Water

			Cyanuric Acid Decomposed in 1 Min.
5	Run No.	Temp. °C	%
	1	190	0.8
	2	200	3.2
10	3	225	28.5
	4	250	100.0

TABLE II  
Decomposition of 20% Slurries of  
Cyanuric Acid in 20% Phosphoric  
Acid

			Cyanuric Acid Decomposed in 1 Min.
15	Run No.	Temp. °C	%
	5	190	0.2
	6	200	0.9
	7	225	12.0
	8	250	100.0

## WHAT WE CLAIM IS:—

1. A process for high pressure thermal hydrolysis of acid waste water streams containing a compound selected from cyanuric acid, melamine, ammeline and ammelide, the

waste streams having a pH of from 0 to 6 which comprises heating the waste water streams in a pressure vessel at a temperature of from 225°C to 275°C under the auto-generously developed pressure, and continuing the heating for from one minute to 15 minutes, until the compound has been hydrolyzed into ammonia and carbon dioxide.

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2. A process as claimed in claim 1 in which the temperature selected for heating the waste water streams is from 245°C to 275°C.

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3. A process as claimed in claim 1 or 2 in which the time for heating the waste water streams at the selected temperature is from 1 minute to 5 minutes.

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4. A process as claimed in any of claims 1 to 3 in which the ammonia is converted to at least one ammonium salt of the acid present in the acid waste water streams.

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5. A process for high pressure thermal hydrolysis of acid waste water streams substantially as hereinbefore described with particular reference to any of the foregoing Examples.

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